Indian J. Phys. **79(4)**, 361-366 (2005)

AN INTERNATIONAL JOURNAL
IJP

A thermally stimulated depolarization current investigation of poly (phenylene oxide) : poly(styrene) polymer blends

Tulika Mitra, J M Keller* and R Bajpai

Department of Postgraduate Studies and Research in Physics, Rani Durgvati Vishwavidyalaya, Jabalpur-482 001, Madhya Pradesh, India

E-mail : jhoom_mitra@yahoo.com

Received 21 August 2004, accepted 16 February 2005

Abstract : A thermally stimulated depolarization current (TSDC) investigation in short circuit configuration has been carried out on physical blends of an amorphous polymer poly(phenylene oxide) (PPO) and semicrystalline polymer poly(styrene) (PS). Blends of composition PPO : PS :: 95 : 05; 90 : 10; 85 : 15 and 80 : 20 were polarized at various temperatures ranging from 308 to 383 K with fields 100, 150, 160 and 190 kV/cm. The depolarization currents recorded as a function of temperature and field were characterized by two well defined peaks. The low temperature peak observed in the temperature range 323–338 K has been identified as the manifestation of the dipolar processes associated with the orientation of molecular dipoles attached to the phenyl groups. The high temperature peak appearing in the temperature range 343–363 K is a complex relaxation process associated with the motion of excess charges together with dipolar reorientation. The anomalous character of the TSDC under certain condition of field and temperature is considered due to detrapping of excess charge carriers in large number resulting in partial blocking of polymer-metal interface.

Keywords : Thermally stimulated depolarizing current, polymer blends, electrets, anomalous current

PACS Nos. : 77.22.Ej, 72.80.Le

1. Introduction

Polymers are capable of storing charge permanently when subjected to field temperature treatment. Such quasi-permanently charged dielectrics are then referred to as electrets [1]. The application of amorphous or semi-crystalline polymers as electrets, however, requires the knowledge of conductivity of polymers, of their charge storage capability and of charge decay as a function of time and temperature. It has also been established that electret properties depend on the details of the structure and dynamical properties of the polymers, at both molecular and supermolecular levels [1,2]. Appropriate model systems are however, required to obtain unambiguous and definite conclusions about the structure-property relationship. Blends of two chemically different polymers that are partially compatible, comprise such model systems.

The physical blends of poly (2,6-dimethyl-1,4 phenylene oxide) (PPO), a polyether, and polystyrene (PS) are well known and comprise a class of successful engineering materials. It is the first blend which was found to be miscible over a complete composition range and represents the commercial product with trade name NORYL [3,4]. The two polymers differ strongly in the glass transition temperature that is in their dynamical properties as well as in their structural properties. Initial study of PPO and PS blends yielded inconclusive results in that two distinct phases – PS-rich and PPO-rich phases could be resolved from the dynamical mechanical loss peak measurement [4,5]. The same samples however, exhibit only a single glass transition temperature (T_g) in calorimetric (DSC) measurements [4]. Further studies involving dielectric relaxation showed noticeably broader relaxation than the relaxation for the pure polymers but revealed only the single T_g intermediate between those observed for the blend components [6]. It was concluded that while certain level of miscibility occurred, compositional fluctuations were prevalent enough to yield data indicating definite level of micro-heterogeneity [4].

*Corresponding Author

Thermally stimulated depolarization current (TSDC) is a sensitive technique used to investigate microscopic and macroscopic phenomena with regard to electrically active polymer relaxations, morphology, crystallization and interfacial properties. Alexandrovich and colleagues [7] have applied TSDC techniques to infer basically whether this technique can yield information on the compatibility of PPO/p-chlorostyrene and PPO/PS blend system. They have observed a largely irreducible TSDC peak, which they attributed to the relaxation of oriented dipoles. Kalkar *et al* [8,9] have studied the TSDC behaviour of PPO and observed a temperature and time dependent relaxation peak with distribution in relaxation times. They have also reported that crystalline PPO forms more stable electrets. In the present work, TSDC's in short circuit configuration, have been recorded and thoroughly studied in several PPO/PS blends with the aim to correlate the observed electrical behaviour with the relaxation mechanisms involved.

2. Experimental

The materials used in the present investigation poly(phenylene oxide) and poly(styrene) were obtained from M/S Aldrich chemicals. Blend films about 20 to 90 μm in thickness were prepared by the solvent cast technique on plane glass substrates inside an oven at 333 K using chloroform (AR grade) as the common solvent. Blend films of different compositions were prepared by taking PPO and PS in 95 : 05; 90 : 10; 85 : 15; and 80 : 20 weight % ratio. The samples so prepared were dried in air for 24 hours and then subjected to room temperature outgassing at a pressure of 10^{-4} torr for a further period of 24 hours.

Both the surfaces of such preconditioned samples were then vacuum-aluminized over a central circular area of 50 mm diameter. The samples were thermally polarized with polarizing fields of 100, 150, 160 and 190 kV/cm at temperatures 323, 343, 363 and 383 K. After polarizing for ¾ hrs at the desired temperature, the samples were cooled to room temperature with the step field still on. Total time of polarization was thus adjusted to be 1.5 hrs in each case. The charged samples were subsequently depolarized by reheating them at a linear rate of 3°C/min. The resulting discharge current was monitored using a Keithely electrometer (Type 610 C).

3. Results

(i) Field dependence :

The typical thermally stimulated depolarization current (TSDC) spectra for PPO : PS : : 95 : 05 (wt%) specimen polarized at temperature (T_p) 323 K with various fields E_p, are shown in Figure 1. Curves 1–4 correspond to E_p of 100, 150, 160 and 190 kV/cm, respectively. A depolarization current flowing in the same direction as the charging/polarization current means a positive current, and a positive TSDC is called anomalous since its direction is opposite to the direction usually expected. A current flowing in the direction opposite to the charging current means negative current and normal current.

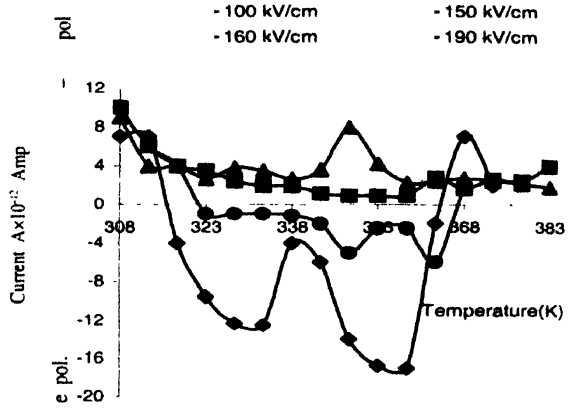

Figure 1. TSDC thermograms for 95 : 05 blend samples polarized at temperature 323 K with various fields : 100, 150, 160 and 190 kV/cm.

The thermograms are characterized by two well defined peaks or humps centered in the temperature range 323-338 K and 343–363 K, respectively. It is observed from the curves that although the specimens were polarized with different E_p values, the position of the current maxima characterized by T_m and corresponding to the peak remains unaltered. For samples polarized with low fields, the TSD current during the high temperature part of the TSDC run was found flowing in the same direction as that during the charging process (positive or anomalous direction) and the two peaks were observed in anomalous direction. However, as E_p was increased, the current was found to become normal and the TSDC peaks were observed in the direction opposite to the charging current. For very high values of polarizing field E_p, the current again exhibited anomalous behaviour and the peaks were observed in the positive direction.

The spectra for PPO : PS : : 85 : 15 (wt%) specimen [Figure 2] exhibited no TSDC peaks. The current was found flowing in the normal sense showing a decrease in magnitude with increase in the values of polarizing field E_p. However, for very high values of E_p, the current was found to exhibit anomalous character during the high temperature part of the TSDC cycle.

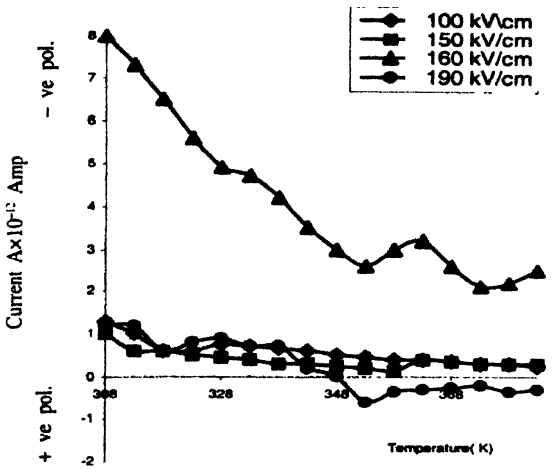

Figure 2. TSDC thermograms for 85 : 15 blend sample polarized at temperature 323 K with various fields : 100, 150, 160 and 190 kV/cm.

The activation energy (E_{act}) was evaluated using the initial rise method of Garlic and Gibson [10] from slopes of the log $I(T)$ *versus* $1/T$ plots. The calculated activation energy values range from 0.35 to 2.48 eV.

(ii) Temperature dependence :

The temperature dependence of TSDC spectra for PPO : PS: : 95 : 05 (wt%) films polarized with a field of 160 kV/cm at different temperatures are shown in Figure 3. The curves 1–4 correspond to T_p of 323, 343, 363 and 383 K, respectively. The thermograms, in general, are characterized by two well defined peaks : a low temperature peak in the range 323–338 K and a high temperature peak in the range 343–363 K. It is evident that as the polarizing temperature was increased, the

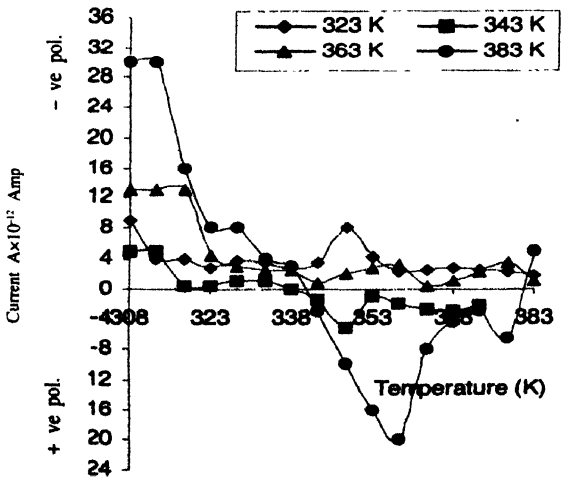

Figure 3. TSDC thermograms for 95 : 05 blend samples polarized with a field of 160 kV/cm at various temperature 323, 343, 363 and 383 K.

magnitude of TSDC decreased and the low temperature peak gradually disappeared.

For specimen polarized with high T_p values, the TSDC was found to flow in the positive direction during the higher temperature part of the TSDC cycle and a prominent single peak of anomalous character was observed. The locations of the two observed peaks were independent of the polarizing temperature.

The temperature dependence of PPO : PS :: 85 : 15 specimen polarized under identical conditions of temperatures and field is depicted in Figure 4.

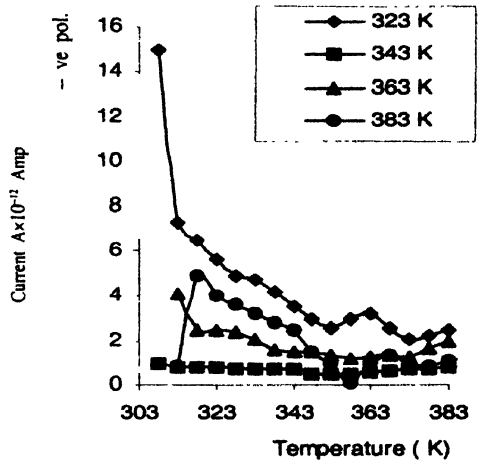

Figure 4. TSDC thermograms for 85 : 15 blend samples polarized with a field of 160 kV/cm at various temperatures 323, 343, 363 and 383 K.

The thermogram did not show characteristic peaks and the TSD current was found to flow in the normal direction opposite to the charging current in all cases. However, the magnitude of the TSDC decreased with increase in T_p at first but was then found to increase for higher values of polarizing temperature.

4. Discussion

Persistent polarization in thermally charged specimen may arise due to various mechanisms, the important among which are dipolar polarization, space charge polarization or transition and trapping of charge carriers at microscopic distances or accumulation near the electrode, and interfacial or Maxwell Wagner effects that is the trapping of charge carriers at phase boundaries. The charge originated in TSDC due to dipolar orientation or trapping of charges in defect or dislocation sites, is known to give rise to a uniform polarization which is hetero-charge. On the other hand, the space charge built up by migration of carriers, mainly ions, over microscopic distances, gives a

non-uniform hetero-charge, whereas trapped injected space charge results in a non-uniform homo- or hetero-charge depending upon the work function of the metal electrodes.

In the present investigation, TSDC thermograms are characterized by two peaks in the temperature range 323–338 K and 343–363 K, respectively as shown in Figure1. Further, the thermally stimulated discharge current in general, is found to flow in the normal direction that is opposite to the charging current. However, in some cases, over certain part of the discharge cycle, it exhibits an anomalous behaviour and flows in the same direction as the charging current. Thus, processes involving hetero-charge formation are mainly responsible for polarization in the blends.

Relaxation processes in crystalline polymers are related to molecular motions of amorphous and/or crystalline chains [11–15]. Usually, two molecular relaxations have been observed in PPO and are labeled as γ and α in order of increasing temperature. The α-relaxation peak observed at high temperature around 503 K (at 100 Hz), has been attributed to the thermal excitation of cooperative motions in chain and identified with the glass transition temperature. The low temperature γ-relaxation peak is observed around 157 K (at 100 Hz) and is attributed to a logically vibration mode of dipolar part [11,15]. De Petris and colleagues [15] have observed an intermediate β-relaxation at 373 K (at 7 KHz), which they have interpreted as due to oscillations of the aromatic rings around the C-O-C bond. The TSDC cycle in the present investigation, has been carried out at the temperatures above room temperature that is 303 K which is much above the temperature of γ-relaxation of PPO or PPO : PS blend. Nevertheless, the high value of initial current observed in all the thermograms, does point towards the existence of at least one relaxation peak at some temperature below 303 K.

The thermograms for the PPO : PS :: 95 : 05 thermo-electrets obtained with polarizing temperature of 323 K and low polarizing field 100 kV/cm, are characterized with peak at 323–338 K and 343–363 K in the anomalous direction. For moderate field values, the current as well as the peaks were observed in the normal direction but for very high field values, the current again exhibited anomalous behaviour with maximum in the positive direction.

The electrets obtained with the fixed field of 160 kV/cm at low polarizing temperature, in general, exhibited the same peaks in the normal negative direction (in case of 343 K, the high temperature peak is observed in anomalous direction). However, with increase in polarizing temperature, the low temperature peak was found to broaden, decrease in magnitude and gradually disappear while the high temperature peak exhibited reversal and was observed in the anomalous direction.

The independence on the polarizing temperature of the position of low temperature peak, indicates that the peak is a manifestation of orientation of molecular side groups. Phenyl rings/methyl groups of PPO are reported to exhibit localized vibrations at temperature sufficiently lower than T_g. PS is also reported to exhibit four small maxima associated with the oscillation of phenyl groups [16–18]. The dipoles attached to the phenyl groups of both the polymers are oriented by the applied field resulting in a current peak located in the temperature range 323–368 K. It appears at sufficiently high polarizing temperatures that the interaction between the phenyl groups of PPO and PS becomes sufficiently intense. As a consequence of this, the molecular dipoles are entangled in such a way that their total contribution to the TSDC becomes insignificant.

The activation energy associated with the low temperature peak ranging from 0.35 to 0.7 eV can be considered in good agreement with the order of activation energy required for the rotation of dipoles/molecules in many long chain polymers. The broadening of the peak indicates that the relaxation process is a distributed process involving dipoles with a distribution in relaxation time rather than dipoles with a single relaxation time.

The high temperature peak observed in the present investigation is probably a complex relaxation process. In addition to dipoles, it can be attributed to the motion of excess charges that is either the drift of space charges into sample or to the neutralization by intrinsic charge carriers. In either case, it is the conductivity of the material that controls the motion of the charges as the function of temperature. The TSDC peak will occur at a temperature for which the relaxation time characteristics of the motion of charge will correspond to the characteristic time scale of the experiment. This is of the order of 10^{-3} s^{-1} so that the peak expectedly occurs at temperature for which the conductivity of various blends are approximately identical.

PPO being a linear polymer, largely amorphous in character, the charge storage and transport in it is expected to be dominated by various localized levels in the amorphous regions and also at the crystalline-amorphous

inter phase/boundaries. Further, since it is a polar polymer, the probability of the presence of intrinsic charge carriers in it, is also sufficiently high, particularly at high temperatures. Incidentally in heterogeneous hetero-electrets of PPO and PPO : PS blends, these charges will mainly pile up at the phase boundaries. They are supplied there by unequal ohmic conduction currents within the two phases (Maxwell-Wagner charging). These carriers are also likely to be trapped in the different trapping sites leading to space-charge effect, which fundamentally influences all charging, and transport processes in such system. Their high concentration often enables them to contribute significantly to the short circuit TSDC.

The magnitude of the peak current is found to decrease with increase in the polarizing temperature and for electrets obtained with high polarizing temperatures, the current and the peak exhibit anomalous behaviour. The observed high values of activation energy and the nonlinear variation with the polarizing field of the charge associated with the peak (curves not shown), indicate that space charge and charge trapping effects are also responsible for this high temperature relaxation observed in the present case.

In general, the decay of space charges in heterogeneous system is ascribed to ohmic dissipation alone, any motion of charge is neglected. They are considered to be neutralized by opposite charge carriers replenished at the phase boundaries by unequal ohmic conduction current (Maxwell-Wagner discharging). The occurrence of interfacial space-charge polarization requires that there be enough carriers of a sufficiently high mobility, which are expected at temperatures above room temperature in the present case, when the ohmic conductivity is sufficiently high. The observed activation energy values 1.2–2.48 eV for the high temperature peak also agrees fairly well with the activation energy for ohmic conduction, which amounts to ~2.0 eV.

The anomalous TSDC's flowing in the same direction as the charging current has been reported by a number of workers [19–21]. The anomalous TSDC's observed under certain conditions of charging field and temperature in the present case, can be understood to be due to space charge formation and partial blocking of the metal-polymer contact as suggested in the literature [19–21]. Considering one type of carriers, electrons for example, we may have a distribution of charge carriers just after charging. The concentration of trapped charge carriers is highest near the charging electrode and decreases with the distance towards the other electrode. Usually, the carriers move towards the nearest charging electrode (outflow) and recombine with their image charges on the electrode. The discharge current has its normal hetero direction. However, if the charge carrier return rate towards the nearest electrode exceeds the charge carrier exchange rate at the electrode, the carrier will diffuse and inflow towards the further electrode- generating a positive current. This may partly cancel or even exceed the negative space charge-limited drift current, thus leading to the striking current reversal. Obviously, diffusion only becomes significant for large gradients which may be found particularly in hetroelectrets of blends of amorphous polar polymers PPO and semicrystalline polymer PS.

In the present investigation, the high temperature current peak exhibits anomalous behaviour for thermo-electrets obtained with various polarizing fields and charged at high temperature. In case of electrets obtained at $T_p \sim 323$ K with low E_p values, the peak shows anomalous behavior. However as E_p increases, current becomes normal, but becomes anomalous again for very high values of E_p. This can be understood as follows. The polarizing temperature $T_p \simeq 323$ K can be considered high enough to provide carriers that occupy shallow traps available with small de-trapping times. Rather easier release of such carriers in large numbers, is supposed to cause a high return rate of carriers from the traps to the nearest probing electrode resulting in partial blocking of the electrode which leads to the anomalous current discharge for such samples. As the step field is increased, the density of carriers is increased. With high mobility and under the influence of a strong internal field, the carriers are transferred to the deeper traps with long de-trapping times. Obviously, the release of carriers from such deeper traps is not expected to result in a carrier return rate sufficient enough to cause blocking of the probing electrode so that the discharge current has its normal hetero-direction. For very large values of step field, the shallow as well as deep traps are filled. The de-trapping of very large number of carriers from shallow traps during the discharge cycle, results in a positive current which is therefore, anomalous in character.

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